

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C08F 255/02, C08G 67/02	A1	(11) International Publication Number: WO 99/01488 (43) International Publication Date: 14 January 1999 (14.01.99)
(21) International Application Number: PCT/US98/13611 (22) International Filing Date: 30 June 1998 (30.06.98) (30) Priority Data: 97201992.1 1 July 1997 (01.07.97) EP (34) Countries for which the regional or international application was filed: AT et al. (71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): ROLLAND, Loic, Pierre [FR/FR]; Residence Metna, 234, avenue de la Grande Champagne, F-01220 Divonne-les-Bains (FR). BOISSON, Melanie, Béatrice [FR/FR]; Batiment C, 715, rue Voltaire, F-01220 Divonne-les-Bains (FR). (74) Agent: KELLY, Patricia, L.; E.I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: AU, BR, CA, CZ, JP, KR, SG, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: POLYOLEFIN COMPOSITIONS (57) Abstract Nonhalogen-Containing Thermoplastic Polyolefin blends are provided which are either heat resistant and are particularly useful in wire and cable coatings, extruded profiles, sheet form or injection molded part or have an elastomeric behavior and are particularly useful in injection molded part. These blends comprise preferably (1) ethylene n-butyl acrylate glycidyl methacrylate (EnBAGMA) terpolymer, (2) an ethylene propylene rubber (EPDM) grafted with maleic anhydride, (3) a polypropylene homopolymer for heat resistance or a very low density polyethylene for elastomeric behavior or a linear low density polyethylene (LLDPE) or a low density polyethylene or a high density polyethylene or an ethylene-polypropylene copolymer.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Title

Polyolefin Compositions

5

Background of the Invention

Field of Invention:

10

This invention relates to polyolefin compositions and more particularly to such compositions which have good heat performance or elastomeric characteristics, and to shaped articles made from them.

Background Discussion:

Polyvinyl chloride (PVC) compositions have been on the market for many years and are commonly used in a large variety of applications. With the trend toward a chlorine-free environment, there is in some market segments such as construction, automotive and wires and cables industries a need for an alternative to PVC. Crosslinked polyolefin compounds or blends of fluoropolymers and PVC have been proposed, though both solution tend to be expensive

WO 93/19118 and WO 89/06256 disclose PVC-free compositions that are suitable for use as coatings for electrical cables. These compositions contain several components that are similar to those described, but lack, i.a., the terpolymer described in the present application.

EP 0 703 271 A1 discloses flexible, halogen-free thermoplastic polyolefin compositions, including certain which are based upon ethylene vinyl acetate, ethylene vinyl acetate carbon monoxide and very low density polyethylene. While these compositions are useful in many applications, they have been found to soften or melt unacceptably under certain high temperature applications.

35

Summary of the Invention

According to the present invention there is provided a polyolefin composition which has good heat performance or elastomeric characteristics, is free from halogen-containing and comprises a blend of:

- (1) ethylene n-butyl acrylate glycidyl methacrylate terpolymer containing 30-90% by weight ethylene, 10-70% by weight n-butylacrylate and 0.5-30% by weight glycidyl acrylate or methacrylate,
- (2) a polyolefin or rubber selected from the group consisting of (a) ethylene propylene diene methylene rubber (EPDM), (b) a linear low density polyethylene, (c) an ethylene-propylene copolymer, and (d) a very low density polyethylene, or a blend thereof; each of which is grafted with 0.05-3 % by weight of a carboxylic acid or any anhydride thereof, and
- (3) a polyolefin selected from the group consisting of (a) polypropylene homopolymer, (b) very low density polyethylene (c) linear low density polyethylene (d) low density polyethylene (e) high density polyethylene and (f) ethylene-polypropylene copolymer.

Common additives which may be included in the composition of the present invention include brominated fillers, aluminium trihydrate or magnesium hydroxide for flame retardancy, antioxidants, titanium dioxide (for UV resistance and to give a white color to the product), processing aids like zinc stearate and UV stabilizers.

Detailed Description of the Invention

The present invention relates to heat resistant non-halogen containing thermoplastic polyolefin blends which are useful in wire and cable coatings, extruded profiles, sheet form or injection molded parts, as well as to elastomeric thermoplastic polyolefin blends which are useful in injection molded parts. These blends generally are formed by combining an ethylene n-butyl acrylate glycidyl methacrylate (EnBAGMA) terpolymer, polymer or rubber grafted with maleic anhydride and a polyolefin all of which are chlorine free.

Polymer blends according to the present invention can be formed in wire and cable coatings, extruded profiles, sheet form or injection molded parts which have many properties comparable to polyvinyl chloride (PVC) containing blends, but with better resistance to heat than polypropylene.

Unless otherwise stated, percentage weight ranges for each of the components in the composition of the present invention are calculated exclusive of any additives which may be present.

The EnBAGMA terpolymer (component (1)) useful in this invention preferably contains 30-90% by weight ethylene, 10-70% by weight nbutylacrylate and 0.5-30% by weight glycidyl acrylate or methacrylate, more preferably 50-80% by weight
5 ethylene, 20-35% by weight nbutylacrylate and 0.5-10% by weight glycidyl methacrylate or acrylate. In general, these EnBAGMA's have a melt flow index (MFI) in the range of 1-50 g/10 min., preferably in the range of 5-20 g/10min. as determined by ASTM D-1238 (measured at 2,16 kg and 190 °C) and are well-known in the art.

10 Component (1) preferably comprises 1-40% by weight of the composition of the present invention, more preferably 5-25% by weight, still more preferably 10-20% by weight.

The grafted polyolefin or rubber (component (2)) useful in this invention is preferably
15 EPDM grafted with 0.05-3 % by weight of maleic anhydride. In general, these EPDM's have a melt flow index (MFI) in the range of 0.05-100 g/10 min., preferably less than 20 g/10min. as determined by ASTM D-1238 (measured at 2,16 kg and 190 °C) and are well-known in the art.

20 Component (2) preferably comprises 5-60% by weight of the composition of the present invention, more preferably 10-40% by weight, still more preferably 20-30% by weight.

The polyolefin (component (3)) will be chosen according to whether heat performance
25 or elastomeric properties are more important for the end use of the composition, as will be known to one skilled in the art. In general, polypropylene homopolymer (PP) is preferred where heat performance is most important, and very low density polyethylene (VLDPE) is preferred where elastomeric characteristics are most important. Linear low density polyethylene (LLDPE), high density polyethylene
30 (HDPE), low density polyethylene (LDPE) and ethylene-propylene copolymer (E-PP) will be used for end uses requiring heat performance or elastomeric characteristics that are not extreme.

The terms of VLDPE and LLDPE includes copolymers of ethylene and other alpha-
35 olefins such as 1-butene, 1-hexene, and 1-octene. The processes for producing VLDPE, LLDPE, HDPE, LDPE, PP and E-PP are well known in the art and commercial grades of these polyolefins are available.

Component (3) preferably comprises 20-90% by weight of the composition of the present invention, more preferably 40-70% by weight, still more preferably 50-60% by weight.

- 5 In addition to its polymer components, the composition of the present invention can be blended with maleic anhydride grafted polyolefins as compatibilizers and/or with common additives such as reinforcing and non-reinforcing fillers, flame retardant fillers such as brominated fillers, magnesium hydroxide, aluminium trihydrate, antioxidants, UV stabilizers, lubricants (e.g., oleamide), antiblocking agents, antistatic
10 agents, waxes, coupling agents for fillers, pigments, titanium dioxide, talc and other processing aids (e.g., zinc stearate) known in the polymer compounding art. The pigments and other additives may comprise up to about 70 weight percent of the total composition based on polymer components plus additives (the polymer components being present in amounts with respect to each other in the proportions previously
15 specified); preferably pigments and fillers comprise above about 0 to about 70 weight percent of the total composition.

- The blends of the invention can be prepared by mixing the polymeric ingredients and optional additives by use of conventional masticating equipment, for example, a
20 rubber mill, Brabender Mixer, Banbury Mixer, Buss-ko kneader, Farrel continuous mixer or twin screw continuous mixer. Mixing times should be sufficient to obtain homogeneous blends and reaction between the glycidyl methacrylate groups of EnBAGMA and the maleic anhydride of the grafted polymer (component 2). Satisfactory mixing times depend upon the type of mixing equipment (shear
25 intensity). Typically, mixing times of about 5 minutes are satisfactory on a batch mixer (Banbury) while 1.5 -2 minutes are satisfactory on a continuous mixer (Brabender, Buss ko-kneader, Farrel or twin screws). If the polymer blend is obviously non-homogeneous, additional mixing is required.

- 30 The invention can be further understood by the following examples in which parts and percentages are by weight or in parts per hundred rubber (phr) and temperatures are in degrees Celsius.

Examples 1-4Legend

- 5 MFI = melt flow index
EnBAGMA = ethylene n-butylacrylate glycidyl methacrylate
EPDM = ethylene propylene rubber
MAH = maleic anhydride
VLDPE = very low density polyethylene
10 LLDPE = linear low density polyethylene
PP = polypropylene homopolymer

Procedure

- 15 A blend is prepared by melt-compounding the following components in the proportions set forth in Table 1 below.
- EnBAGMA (66.75% ethylene, 28% n-butylacrylate and 5.25% glycidyl methacrylate) having a MFI (190°/2.16 kg) of 12
 - 20 • MAH grafted EPDM (2% MAH) having a MFI (190°/2.16 kg) of 2.0
 - PP having a MFI (230°/2.16 kg) of 21
 - MAH grafted PP (0.55% MAH) having a MFI (190°/2.16 kg) of 250
 - MAH grafted LLDPE (0.85% MAH) having a MFI (190°/2.16 kg) of 40
 - VLDPE having a density of 0.870 and a MFI (190°/2.16 kg) of 30
 - 25 • Brominated flame retardant filler (SAYTEX 120)
 - Antimony trioxide flame retardant filler (FSPO 405) available from Chemetron
 - antioxidant - phenolic type available under the name IRGANOX 1010 from Ciba
 - Zinc stearate
- 30 Melt compounding is carried out on a two roll mill with batches from 100 grams at 170-190°C for ca. 5 minutes. The milled product is formed into a testing plaque in a hydraulic press at 170-190°C for 5 minutes. Afterwards stress-strain (tensile strength-tensile elongation) testing (ASTM D-638) Heat Deformation at 90 and 160 °C (a 30 gr weight is hanged to a plate sample having a thickness of 0.5 mm, a length of 10 cm
- 35 and a width of 10 mm) and permanent set test in tension (ASTM D412) are carried out. Results are shown in Table 1.

Table 1

<u>Example numbers</u>		<u>1</u>	<u>2</u>	<u>Test method</u>
5	EnBAGMA	14	10	
	MAH grafted EPDM	17	25	
	PP	45.6	-	
	VLDPE	-	49.8	
	MAH grafted PP	9.0	-	
10	MAH grafted LLDPE	-	15	
	Brominated filler	10	-	
	Antimony trioxide	4	-	
	Antioxidant	0.4	0.2	
15	Tensile strength	18 MPa	11 MPa	ASTM D 638
	Tensile elongation	250 %	590 %	ASTM D 638
	Heat def. at 90°C	0 %	0 %	(defined in text)
	Heat def. at 160°C	0 %	molten	(defined in text)
	Permanent set in tension	-	20 %	ASTM D 412
20	Shore A hardness	-	80	ASTM 2240
	Specific gravity	-	1.05	ASTM 792
	Compression set at 23 °C	-	26 %	ASTM D 395-89
	Compression set at 100 °C	-	71 %	ASTM D 395-85
	Brittleness temperature	-	-80 °C	ASTM D 1043
25	Tension set at 23 °C	-	22 %	ASTM D 412

One can see that the formulation containing PP shows no deformation at 160 °C and therefore has a particularly good resistance to heat deformation which is a major benefit for automotive primary wires. On the other hand, the formulation containing VLDPE shows a relatively high permanent set value which means good elastomeric behavior which is of interest for injection molded parts.

Claims

1. A flexible, halogen-free polymer composition comprising a blend of
 - 5 (1) ethylene n-butyl acrylate glycidyl methacrylate terpolymer containing 30-90% by weight ethylene, 10-70% by weight n-butylacrylate and 0.5-30% by weight glycidyl acrylate or methacrylate,
 - 10 (2) a polyolefin or rubber selected from the group consisting of (a) ethylene propylene diene methylene rubber (EPDM), (b) a linear low density polyethylene, (c) an ethylene-propylene copolymer, and (d) a very low density polyethylene, or a blend thereof; each of which is grafted with 0.05-3 % by weight of a carboxylic acid or any anhydride thereof, and
 - 15 (3) a polyolefin selected from the group consisting of (a) polypropylene homopolymer, (b) very low density polyethylene (c) linear low density polyethylene (d) low density polyethylene (e) high density polyethylene and (f) ethylene-polypropylene copolymer.
- 20 2. A blend according to claim 1 wherein component (1) comprises 1-40% by weight of the blend, component (2) comprises 5-60 % by weight of the blend, and component (3) comprises 20-90 % by weight of the blend.
- 25 3. A blend according to claim 1 wherein component (1) comprises 5-25% by weight of the blend, component (2) comprises 10-40% by weight of the blend and component (3) comprises 40-70% by weight of the blend.
- 30 4. A shaped article formed from a blend according to claim 1.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/13611

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C08F 255/02; C08G 67/02

US CL :525/63, 71, 74, 185, 190

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 525/63, 71, 74, 185, 190

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,434,217 A (SPELTHANN) 18 July 1995.	1-4
A	US 5,395,881 A (SPELTHANN) 07 March 1995.	1-4
A	US 4,157,428 A (HAMMER) 05 June 1979.	1-4

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"A" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

13 SEPTEMBER 1998

Date of mailing of the international search report

22 OCT 1998

 Name and mailing address of the ISA/US
 Commissioner of Patents and Trademarks
 Box PCT
 Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

BERNARD LIPMAN

Telephone No. (703) 308-0661